

TITANIUM AS A TRACER FOR DETERMINING COAL BURNOUT

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INTRODUCTION

Background. Extensive research on coal combustion at this laboratory (1-6) has focused on developing an understanding of the physical and chemical mechanisms and reaction rates of coal burnout and nitrogen and sulfur pollutant formation. Local samples of combustion products have been extracted from the pulverized coal combustor using water-quenched sample probes. To complete mass balances and determine important local parameters, chemically inert tracers have been used in the reactor. Argon added to the primary air has been used as the gas phase tracer to determine the mixing rates of the primary and secondary air streams and the volume of combustion gases from the coal. Carbon conversion is also determined from gas composition, coal feed rate, and a forced argon balance.

Coal burnout has been calculated from the percent ash in the residual char and in the raw coal in previous phases of this study (4-6). However, the use of ash as a particle tracer has not been satisfactory. Ash is not a suitable tracer because it contains many inorganic compounds which decompose and/or vaporize. Kobayashi, et al. (7) and Sarofim, et al. (8) have shown that as much as 20-60 percent of the original coal ash can be volatilized depending on the temperature history of the ash.

Collecting samples of combustion products with a water-quench probe produces a char-water mixture which is filtered and dried to obtain the solid char sample. Many constituents of ash are soluble in the water and more losses are incurred in the total measured ash content. Harding, et al. (6) have shown that up to 10 percent of the ash can be dissolved in the probe quench water.

High losses of ash negate its usefulness as a solid tracer by introducing large errors into the mass balance and burnout calculations. Consequently, there has been an interest in finding another particle tracer which could more accurately determine coal burnout, and also to help understand the fate of the ash and slag.

Mims, et al. (9) have characterized the volatilization of ash with temperature. At higher temperatures, compounds formed from elements such as arsenic, manganese, magnesium, sodium and antimony showed strong vaporization trends. Aluminum, silicon and other known refractory compounds also showed significant losses at high temperatures. Compounds formed from such elements as titanium, scandium, barium and lanthanum were found to be more stable. Because of their low concentrations in the coals, scandium and lanthanum were not considered as feasible tracers. Titanium was selected as a possible tracer because it forms relatively stable high boiling point compounds (i.e., TiO , TiC , TiO_2 , Ti_4O_7), and is found in most coals in easily detectable amounts.

Objectives. The purpose of this study was to develop an analytical procedure which could be used to measure the concentration of a solid particle tracer and apply the techniques to representative samples from the pulverized coal combustor. Techniques commonly used to analyze elements in the ash are atomic absorption (AA), instrumental neutron activation analysis (INAA), x-ray diffraction (XRD), and x-ray fluorescence (XRF). XRF was chosen because of the ease of analysis (sample preparation time 10-15 minutes and analysis time of 40-120 seconds), and availability of a suitable instrument. Comparison of AA, INAA and XRF results for

fly ash and coal analysis have been found to give good agreement for most elements (10).

This study was divided into three tasks: (1) set-up and calibration of the XRF instrument in order to measure titanium trace element concentration in char from the combustor, (2) analysis of char samples from combustor tests to determine the usefulness of titanium in the ash as a tracer, and (3) use of the titanium tracer data to compute mass balances and consequently coal burnout.

TEST FACILITIES

A diagram of the pulverized coal combustor with major dimensions is shown in Figure 1. The reactor, with a coal feedrate of about 13.6 kg/hour, was constructed of five interchangeable sections of 33 cm (14 in.) schedule 40 pipe. Each section was 30.4 cm in length and lined with 6.4 cm of castable aluminum oxide refractory. One of the five sections contained a water-quench, traversing probe which was used to sample the flame at different axial locations in the reactor. This section could be interchanged with any of the other sections in order to obtain gas and char samples at various radial and axial locations, effectively mapping the reactor. A more detailed description of the combustor and its supporting facilities has been reported (4-6).

In order to obtain an adequate sample of combustion char for ASTM ash and XRF Ti analysis, a special larger exit sample probe was used. The probe detail of Figure 1 shows the design of the probe tip that permitted centerline char sample collection near the reactor exit without interfering with other combustor experiments. Both probes were similar in design, differing only in size. Complete details on the design and operation of the probes have been documented (6, 11, 12).

INSTRUMENTATION

A Phillips 1410 vacuum path x-ray fluorescence (XRF) spectrometer was used to analyze titanium in the coal samples. XRF is known for the relatively quick sample analysis time and sample preparation time (10). Quantitative measurements of Ti on the XRF required values for five correction factors: detector dead time, background count, peak overlap, absorption corrections, and instrument electronic and power drift. Each factor is briefly discussed below.

Dead Time. Dead time is the time required for the electronics and detector to register one count of radiation. If a second burst of radiation arrives at the detector before the first burst is registered, the second burst will not be registered. The bursts of radiation are assumed to be statistically random and a simple correlation is used to quantify the dead-time correction (13).

Background Counts. Natural scattering of the x-rays causes a small count to be present at every angle on the XRF. The background counts vary non-linearly and compensation is made by estimating the background at the peak using an average of the background at angles below and above the peak.

Peak Overlap. Peaks within one or two degrees of the measured peak may add to the number of counts at the desired peak position. Corrections for these overlaps are made by measuring pure disks of the interfering element and determining the height of the peak at the desired angle.

Absorption and Instrument Drift. Fluorescence from an element within the sample matrix could be absorbed by another element, altering the intensity of the peak of the desired element. Carbon and other lighter elements are strong absorbers at the wavelength of radiation from titanium. This causes major problems when organic concentrations in the char vary from 0 to 94 percent. This problem is circumvented by using the internal standard method of calibration. Instrument drift

on the XRF is caused by variations in the voltage, sample placement, and goniometer accuracy on the machine. These are also compensated by the internal standard method (14).

XRF Calibration. The internal standard method of calibration (14) was chosen as the calibration technique. Scandium as Sc_2O_3 , which has an absorption edge near those of the element being measured, was added to the char sample in a known concentration. Since absorption effects are similar for the two elements, the ratio of the concentrations of the unknown to the standard element was related to the ratio of the intensities by a constant factor A:

$$W_{\text{Ti}}/W_{\text{Sc}} = A C_{\text{Ti}}/C_{\text{Sc}} \quad (1)$$

where A is a constant factor, C_{Ti} and C_{Sc} are the measured counts of radiation at the peaks for titanium and scandium in the sample, respectively. This ratio technique eliminates the need for absorption corrections because the peaks are in the same sample, and the absorption correction factors are nearly equal. Calibration after every third sample prevented major errors due to machine drift. Calibration consisted of analyzing a cellulose blank to determine background factors and then analyzing a NBS fly ash standard (NBS Standard Reference Material 1633a) for titanium to determine the value of A in Eqn. 1.

XRF Error Analysis. The counting statistics and equations for the XRF error analysis are explained in detail by Jenkins and DeVries (13). The arrival of bursts of radiation from the sample can be modeled as a Chi Square distribution which approaches a Gaussian distribution. A total XRF counting error of ± 0.4 percent (relative¹) was realized for the tests conducted. This gave a limit of detection of 45 ppm (mass). The raw coal contained about 400-600 ppm titanium (dry basis), well above the minimum.

The XRF counting errors were very small. The major errors were introduced by the sample preparation techniques. Samples were prepared by weighing 400 mg of char, 40 mg of high purity cellulose and 10 mg of Sc_2O_3 into a small vial with a 6mm glass ball. A commercial dental mixer was used to mix and grind the sample for 3 minutes. The sample was then pressed onto a support with a cellulose backing at $4.58 \times 10^6 \text{ kg/m}^2$. The major errors introduced in weighing the Sc_2O_3 accurately were ± 1 to 2 percent. Increasing the percent Sc_2O_3 did not significantly increase the accuracy because of increased error due to increased scandium counts.

TEST PROGRAM

Fifteen combustor tests were performed at four different values of secondary air swirl number² ($S_g^e = 0.0, 1.4, 3.2, \text{ and } 4.5$), and over a range of stoichiometric ratios³ (SR) of 0.59 to 1.65. The coal used was a Wyoming subbituminous coal with about 5.0 weight percent ash (as received) and 0.8 weight percent titanium in the dry ash. The proximate analysis of the coal gave values of 27.8 percent, 32.9 percent, 34.3 percent, and 0.4 percent for moisture, volatiles, fixed carbon, and

¹Relative error is error divided by percent titanium present times one hundred.

²Swirl number (S_g^e) is defined as the flux of angular momentum divided by the product of duct radius and axial flux of momentum.

³Stoichiometric ratio (SR) is defined as the air/fuel ratio divided by the stoichiometric air/fuel ratio. SR values less than one are fuel rich while SR values greater than one are oxidizer rich.

sulfur respectively. The ultimate analysis on a dry basis gave 6.9 percent ash, 4.4 percent hydrogen, 76.3 percent carbon, 1.1 percent nitrogen, 0.5 percent sulfur and 10.8 percent oxygen. The char sample probe was located on the center line of the reactor near the reactor exit (ca 150 cm from the burner inlet). Coal burnout was determined at each test condition from ASTM analysis of the ash sample, and by XRF analysis for titanium in the char sample.

TEST RESULTS

Coal burnout results determined from a titanium mass balance in the char samples obtained are shown in Figure 2. Coal burnout was shown to be primarily a function of stoichiometric ratio, increasing from about 80-87 percent at $SR = 0.6$ (fuel rich) to greater than 95 percent at $SR > 1.1$ (Figure 2(a)). The tests were not all conducted at a consistent set of stoichiometric ratios. Nevertheless, interpolation of the curves (Figure 2(a)) at $SR = 0.6, 0.9$, and 1.2 has permitted the effect of swirl in the secondary air stream to be determined (Figure 2 (b)). The effect of stoichiometric ratio is still quite pronounced. The effect of secondary swirl on coal burnout is small. The combustion of pulverized coal is very complex and the influences of secondary swirl, mixing rate, stoichiometric ratio, etc. are just beginning to be understood (1-6).

An ASTM analysis of the char samples for ash and titanium as a tie component are given in Figure 3. Titanium burnout is higher in every case than the ash burnout, indicating that titanium is a better tracer than ash.

The extent of ash loss, equivalent to an ash burnout, has also been determined from the titanium data. A set of parametric ash loss lines have also been constructed on Figure 3 for comparison (10 percent, 20 percent, 30 percent, 40 percent, and 50 percent). Ash losses of 15 to 60 percent can be observed by the superposition of the data on the various ash loss lines. The extent of ash loss is large compared to earlier work at this laboratory with a bituminous coal (6). However, the difference in coal type, ash composition, and moisture level could account for these differences.

Ash loss has little effect on coal burnout at very high burnout levels. Figure 4 shows the error in burnout due to ash loss at several different burnout levels. At burnout values of 95 percent, ash losses of 40-50 percent create differences of only 2-3 percent in burnout estimates. Hence at moderate ash loss (20-40 percent) and high burnout values (greater than 95 percent burnout) the ash tracer burnout values are almost as accurate as the titanium-based burnout values. However, if burnout is below 95 percent then burnout based on titanium gave significantly improved results.

Asay (12) has recently completed a set of pulverized coal combustion tests at the same secondary swirl numbers and at nearly the same stoichiometric ratios for this Wyoming coal. Carbon burnout data obtained from these tests with a complete gas composition and an argon tracer mass balance are compared in Figure 5 to the titanium analysis coal burnout data reported above. In general, coal burnout is expected to be from 1-2 percent higher than carbon burnout because of the more complete release of the hydrogen from the coal. In general, the agreement between burnout values from the gas analysis and from the titanium analysis is good at $SR > 0.9$. At $SR = 0.6$ however, the burnout values determined from the gas analysis are much lower. Asay (12) is still reviewing this discrepancy but it is thought that the data from the titanium analysis are superior. One possible explanation is that the gas data represent an integration of radial gas composition profiles near the reactor exit while the titanium data are based on centerline samples.

CONCLUSIONS

Titanium can accurately be determined in char samples by using the internal standard method of XRF calibration. Errors of ± 2 -3 percent are incurred mostly from sample preparation inaccuracy. X-ray fluorescence instrument error is less than ± 0.4 percent.

Titanium compounds in ash are more stable than the total ash constituents and hence provide a solid phase tracer to complete overall mass balances with increased accuracy. Burnout calculations are improved by as much as 20 percent at burnout values less than 95 percent and with high ash loss. When coal burnout level is above 95 percent, titanium provides only 1-2 percent increased accuracy in the burnout calculation.

Use of the titanium tracer also provides a method of calculating ash loss. Up to 60 percent of the ash was lost in these combustion tests. This loss is the sum of the losses due to vaporization in the flame and dissolution into the quench water.

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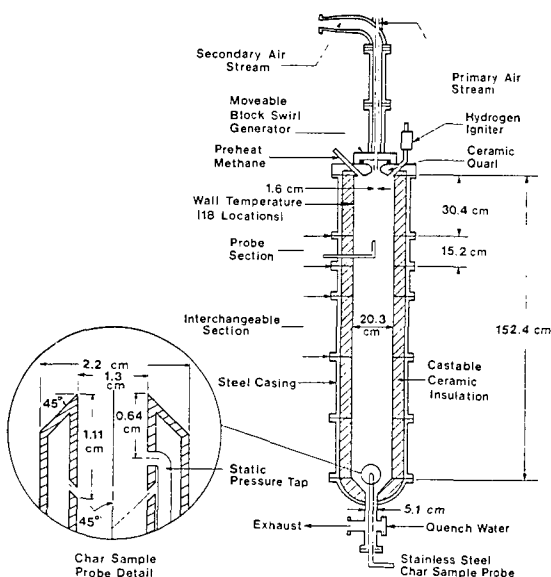


Figure 1. Schematic of atmospheric combustor (Adapted from Harding (6)).

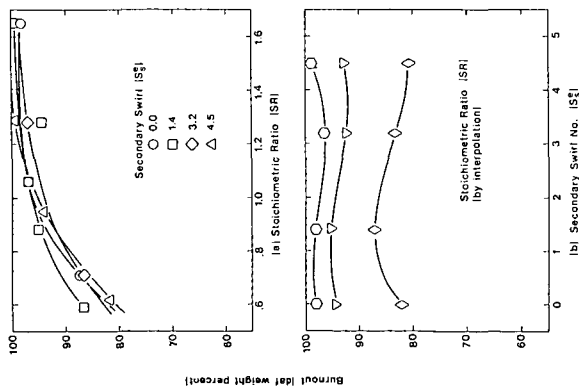


Figure 2. Effect of stoichiometric ratio and secondary swirl number on coal burnout by titanium analysis.

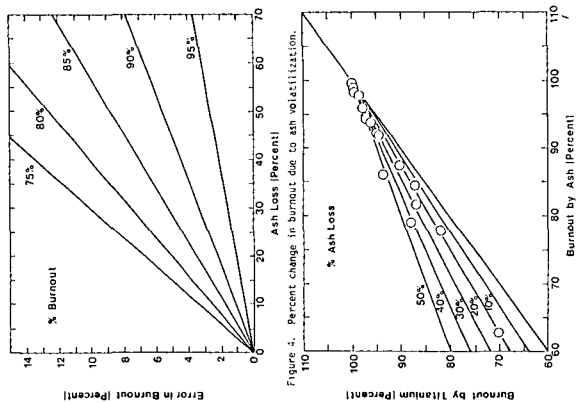


Figure 3. Burnout using titanium compared with burnout using ash as tracer.

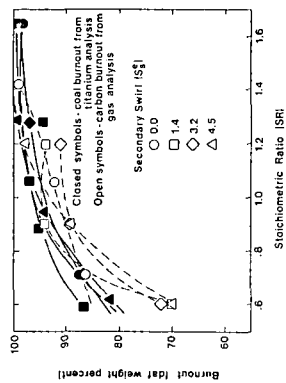


Figure 5. Comparison of carbon burnout by gas and analysis and coal burnout by ash tracer.